Synthesis of Urea from Ammonia and Carbon Dioxide[1]

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The following paper describes the development of a process for the synthesis of urea from ammonia and carbon dioxide. The process consists in the preparation of ammonium carbamate, autoclaving to cause partial conversion to urea, distillation of the resulting sludge to separate the urea from the unconverted ammonia and carbon dioxide, and condensation of the distillate with additional gas to form a new charge. A small-scale experimental plant for testing the process was built and operated.

A discussion of the conversion reaction from a theoretical standpoint is given.

Cost considerations lead to the conclusion that the cost of urea by this process would be largely dependent on the cost of ammonia. It seems possible that the process might have commercial significance for the production of urea for fertilizer purposes, and in any case the process is of interest for the production of urea for its present uses in the arts.

LIMITATIONS on the use to which urea has been put may be ascribed almost entirely to the difficulties and cost attendant upon its commercial production. In recent years the greater part of the urea manufactured in this country has been produced from crude calcium cyanamide. The present cost of urea obtained in this manner limits its use to high-grade products.

The chemical characteristics of urea make it adaptable in many arts; its suitability as a stabilizer in explosive mixtures, as a constituent of varnishes and an ingredient in the transparent celluloid used for photographic films, as a factor in organic syntheses and medicinal preparations is outstanding evidence of the usefulness of urea in technical processes. In recent years, other uses for urea have been discovered, the developments of which have been checked by cost considerations. Foremost among these latent possibilities is the use of urea for fertilizing purposes. Many references[2] could be cited showing the value of urea as a nitrogenous fertilizer. It is logical to infer that greater and more varied uses for urea await improvements in methods for its synthesis.

The materials required in the process herein described are ammonia and carbon dioxide. Sources of ammonia are by-product coke ovens and nitrogen fixation plants using either the cyanamide or Haber process. Carbon dioxide is a waste product of many industries and can readily be concentrated if necessary. It should be pointed out, however, that a plant for the synthesis of ammonia by the Haber-Bosch process, in which hydrogen is produced by the water-gas reaction, also supplies carbon dioxide in large amounts. The gas coming from the water used in scrubbing the nitrogen-hydrogen mixture contains 70 to 80 per cent carbon dioxide and seems entirely adaptable for use in the synthesis of urea by the process to be described. Carbon dioxide may also be obtained from limekiln gas, which contains 15 to 40 per cent carbon dioxide, depending on the type of kiln or retort. The carbon dioxide content of the gas may be increased by absorption in water at moderate pressures (25 atmospheres) exactly as carried out in the water scrubbers of a Haber plant.

[1] Received March 8, 1922.

[2] *Mitt. deut. Landw. Ges.*, **31** (1916), 16, 90; *Jahrb. deut. Lande. Ges.*, **34** (1919), 305; *Wochschr. Brau.*, **36** (1919), 355.

PREVIOUS WORK

Basaroff,[3] in 1870, found that "considerable" quantities of urea could be obtained by heating ammonium carbamate in sealed tubes at a temperature between 130° and 140° C. He also found that commercial ammonium carbonate is partly converted to urea by similar treatment, but no yields are given. Herroun,[4] in 1881, discovered that urea and ammonium cyanate are formed when a mixture of air with the vapors of benzene and ammonia solutions is passed over a heated platinum wire and subsequently cooled. These experiments were performed in simple laboratory apparatus and yielded only sufficient product to serve for analysis. Mixter,[5] in 1882, synthesized urea from ammonia and carbon dioxide by passing the mixed gases through a hot tube at atmospheric pressure. Urea was formed at the rate of 10 to 15 mg. per hr.; the quantity of ammonia used per hour is not stated, however. Bourgeois,[6] in 1897, carried out experiments very similar to those of Basaroff, and by alternate heating and cooling with release of pressure managed to obtain a 6 per cent conversion to urea. Finally, in 1911, the reaction was investigated quite thoroughly by Fichter and Becker.[7]

THEORETICAL CONSIDERATIONS

In August 1919, this Laboratory began an investigation of the synthesis of urea from ammonia and carbon dioxide. Preliminary experiments were performed with ammonium carbamate, which was made by passing ammonia gas and carbon dioxide into absolute alcohol according to the method of Mente.[8] The ammonium carbamate was sealed in heavy glass tubes and heated at different temperatures for several hours. After cooling, the contents of the tubes were removed and analyzed for urea. The yields of urea were extremely low. It was later realized that several important factors influencing this reaction were not at first fully appreciated. These factors are brought out by a consideration of the thermochemistry and thermodynamics involved and will be briefly discussed.

The formation of urea from ammonium carbamate is essentially expressed by the equation:

$$(NH_3)_2CO_2 \rightleftharpoons CO(NH_2)_2 + H_2O - \text{heat}$$

Ammonium carbamate — Urea — Water

The equilibrium for this reaction in dilute solutions has been determined by Lewis and Burrows[9] at 77°, 110°, and 132° C. Applying van't Hoff's equation, the data of Lewis and Burrows lead to the value −6400 cal. for the heat of reaction, while Matignon and Frejacques[10] give for the heat of the reaction the calculated value −6000 cal. and state that the experimental value is −7700 cal. The method of

[3] *J. prakt. Chem.*, [2] **1** (1870), 283.

[4] *J. Chem. Soc.*, **39** (1881), 471.

[5] *Am. Chem. J.*, **4** (1882–83), 35.

[6] *Bull. soc. chim.*, [3] **17** (1897), 474.

[7] *Ber.*, **44** (1911), 3473.

[8] *Ann.*, **248** (1888), 235.

[9] *J. Am. Chem. Soc.*, **34** (1912), 1515.

[10] *Bull. soc. chim.*, **31** (1922), 101.

experimentally determining the heat of reaction is not stated. In any case, the data are sufficient to show that the reaction is endothermic and that improved yields of urea will be obtained as the temperature is raised.

Although the data of Lewis and Burrows for the equilibrium in this reaction are undoubtedly satisfactory for dilute solutions, nevertheless the extrapolation of their results to the concentrated "melts" or solutions obtained in actual practice can hardly be very reliable. A very rough calculation can be made, however, on the assumption that the fugacities of carbamate, urea, and water are proportional to the molal fractions of the three substances.

At 132° C., Lewis and Burrows obtained a solution which contained 0.967 g. of carbamate, 0.0331 g. urea, and 1.511 g. of water. Considering the mass law expression where f^1, f^2 and f^3 are the fugacities of carbamate, urea, and water, respectively, we obtain from the data of Lewis and Burrows,

$$K = 0.0385.$$

An analysis[11] was made of a solidified "melt" resulting from heating pure ammonium carbamate at 125° C. in a sealed tube. The total weight of the "melt" was 1.5464 g. Its urea content was 0.4089 g. Since water and urea are formed in equivalent quantities we may take the water content as equal to

$$\frac{18}{60} \times 0.4089 = 0.1227 \text{ g.}$$

Calculating the molal fractions and substituting in the mass law expression, we obtain

$$K = 0.134.$$

It will be noted that even though the temperature is lower than that at which Lewis worked, the equilibrium constant is considerably larger. This must be due to the incorrectness of our assumption that the fugacities of the substances involved are proportional to their molal fractions. In all probability the fugacity of the carbamate increases much more rapidly than its concentration because of the decreased hydrolysis in concentrated solutions. From the point of view of the manufacture of urea by this process it is very fortunate that higher yields can be obtained than would have been predicted from an extrapolation of the data of Lewis and Burrows.

In connection with any attempt to make theoretical calculations as to the yield to be expected it must be noted that the system is really one of great complexity. We have very little information concerning the hydrolysis of ammonium carbamate, and other secondary reactions may occur in the "melt," as will be noted from the following list:

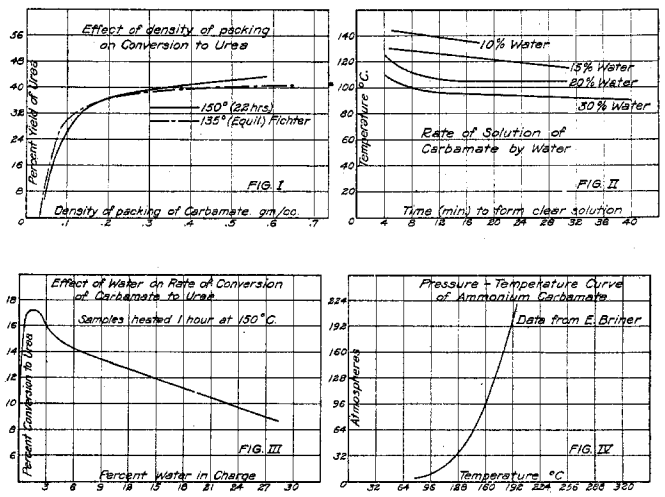
$$(NH_3)_2CO_2 + H_2O = (NH_4)_2CO_3$$
$$(NH_4)_2CO_3 = NH_4HCO_3 + NH_3$$
$$NH_4HCO_3 = NH_3 + CO_2 + H_2O$$
$$(NH_4)_2CO_3 = 2NH_3 + CO_2 + H_2O$$

Further Experimental Work

From the considerations just mentioned we can conclude that the commercial success of the process lies in the ability to utilize solid ammonium carbamate as the starting material and that the highest practicable temperature should be employed. The glass tube experiments were continued in order to determine the influence of other factors. This laboratory was soon able to establish conditions under which a conversion of approximately 40 per cent of the total ammonia to urea could be consistently obtained.

It is evident that since the equilibrium is established in the liquid phase and presumably only a negligible amount, if any, of urea is in the gaseous phase, the extent of conversion is dependent on the ratio of the volumes of liquid and gas phases. Accordingly, experiments were conducted in which the weight of ammonium carbamate in a given reaction volume was varied between wide limits. The density of packing, as measured by the grams of carbamate per cubic centimeter of the volume of the container, was found to be an important factor in determining the yield, as is shown in Fig. I.

Another factor whose influence it was desirable to determine is the per cent of water present in the original carbamate.



In order to obtain some qualitative information on this point, a number of mixtures of carbamate and water were subjected to different temperatures and the time interval necessary to form a clear solution noted. This time interval is a measure of the rate of heat conduction through the mixture, and while it is, of course, dependent on the dimensions of the container, it does give a qualitative measure of the rate of heat transference through the charge. Fig. II shows these results graphically. The effect of water on the rate of the reaction is, of course, intimately connected with this, and the results of experiments in which mixtures containing different percentages of water were heated for 1 hr. at 150° C. are graphically shown in Fig. III. The very rapid increase in the rate of the reaction with the addition of small percentages of water is noteworthy. It is believed that this effect is due primarily to the better heat conductivity of the material containing water. Additions of water greater than about 1.5 per cent apparently result in a partial reversal of the reaction.

The laboratory experiments just described yielded the information that solid ammonium carbamate is the best starting material for the urea conversion reaction and that the yield of urea is markedly dependent on the density of packing of the charge. Qualitative information regarding the effect of water on the rate of heat conductance through the charge and the effect of water on the rate of conversion was obtained. The further developments arising from the operation of a small-scale plant will now be described.

Experiments with Small Experimental Plant

PREPARATION OF AMMONIUM CARBAMATE—Previous workers in this field have used the method of Mente,[8] in which ammonia and carbon dioxide are passed into cold absolute alcohol, ammonium carbamate separating out. The use of absolute alcohol, of course, limits the use of this method to a laboratory scale. Another objection is that it is impossible to remove the last traces of alcohol from the precipitated carbamate. According to Fichter and Becker,[7] traces of alcohol exercise an inhibiting effect on the formation of urea,

[11] The authors are indebted to Messrs. E. J. Fox and L. Pinck of this Laboratory for analytical assistance in connection with this investigation.

but the present writers have not been able to substantiate this. An analysis of their data indicates that more than one influencing factor was varied at one time, and the decreased yield may be in part accounted for by a decreased density of packing.

Other known methods of preparing ammonium carbamate involve the use of nonaqueous liquids in which carbamate is not appreciably soluble, the condensation of gaseous mixtures on cold surfaces, or the use of liquid ammonia and gaseous carbon dioxide.

In view of the fact that this Laboratory was contemplating a series of investigations in which about 10 to 12 lbs. of ammonium carbamate would be used during a single conversion experiment, it was necessary to develop a method for conveniently preparing large quantities of this material. The use of liquid ammonia and gaseous carbon dioxide was thoroughly tested, with several gallons of liquid ammonia at a time. It was concluded that this method of preparation was wasteful of ammonia and too expensive to warrant further consideration. Another factor that largely determined the course of further experiments developed after some conversions had been carried out in the large autoclave. It was realized that the urea formed from ammonium carbamate would be mixed with water and unchanged ammonium carbamate, since an equilibrium had been definitely established at approximately 40 per cent conversion. The logical method of separation was to distil off the ammonia, carbon dioxide, and some of the water, and to recondense the vapors to form ammonium carbamate for a repetition of the conversion reaction. In fact, the whole success of the process of producing urea from ammonium carbamate seemed intimately linked with the development of a condenser to recover the unchanged ammonia for further use in the process. Data on which to base a reliable calculation as to the capacity and efficiency of a condenser were not available. An apparatus suitable for investigating this point was therefore constructed.

CONDENSATION OF MIXTURES OF AMMONIA, CARBON DIOXIDE, AND WATER—The vapor pressure temperature relations of ammonium carbamate at temperatures from 80° to 200° C. have been carefully measured by Briner,[12] whose results are shown graphically in Fig. IV. In order to extend this curve to lower temperatures, data have been collected from other sources, as indicated in Table 1.

TABLE 1—VAPOR PRESSURE OF AMMONIUM CARBAMATE

Temperature ° C.	Vapor Pressure Cm. Hg	Source of Data
0	1.24	M. and F.[1]
10	2.98	M. and F.
20	6.20	M. and F.
30	12.40	M. and F.
40	24.80	M. and F.
50	47.00	M. and F.
55	60.00	M. and F.
60	77.00	M. and F.
77.2	227.00	B.[2]
81.0	240.68	M. and F.
98.5	640.00	B.
100	686.00	M. and F.

[1] Matignon and Frejacques, *Compt. rend.*, **170** (1920), 462.
[2] Briner, *J. chim. phys.*, **4** (1906), 266.

From these data it is possible to calculate by means of the Clausius-Clapeyron equation, the heat of condensation (or vaporization) of ammonium carbamate. Between the temperatures of 80° and 25° C. the heat of condensation as given by this equation is 12,380 cal. per mole (78 g.). The separation of the unchanged carbamate from the urea would probably be effected by distillation at a temperature not exceeding 80° C. because of the instability of urea at higher temperatures. The advantages of condensing carbamate at about 25° C. are obvious. The association of such large quantities of heat with the condensation (or vaporization) of this compound is evidently due to the fact that in addition to the latent heat we must include the heat of combination (or dissociation) of ammonia and carbon dioxide, since the vapor of ammonium carbamate is a mixture of these two separate gases.

[12] *J. chim. phys.*, **4** (1906), 266.

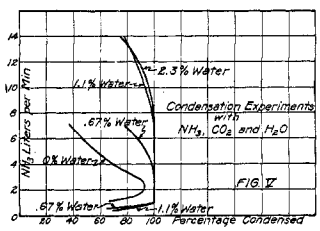
In addition to the necessity of removing such large quantities of heat from the condensate it was known that solid ammonium carbamate is a very poor conductor of heat; consequently the writers were confronted with the problem of removing this heat through a layer of ammonium carbamate which, as previously mentioned, is a very poor conductor of heat. The methods in commercial use for the preparation of similar compounds, such as ammonium carbonate, employ very large surfaces on which the vapors slowly condense. The condensate is removed by breaking off the layers either by mechanically beating the large metal sheets that form the condensing surface or by other similar and equally cumbersome processes. These methods do not appear to be applicable to the present process, especially in the case of small installations where compactness of apparatus is essential. It appeared that a limited surface kept constantly cold, and from which the condensate could be continuously removed by some sort of scraping device, would be a better solution of the problem.

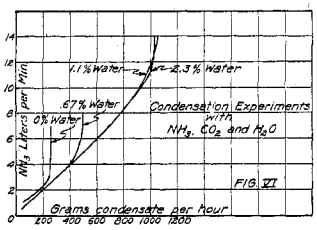
The condenser used in this work was designed to operate on this principle and consisted essentially of a cylindrical tube surrounded by a jacket in which the cooling medium was circulated and provided with a rotating, scraping blade fitting closely inside the cooled tube. The mixed gases, ammonia and carbon dioxide, together with the desired quantity of water vapor, were led into the upper end of this tube and condensed out on the cool walls from which the condensate was continuously removed by the revolving blade.

CONDENSATION EXPERIMENTS—In order to determine the efficiency, capacity, and operating characteristics of the condenser, an investigation of the condensation of measured quantities of ammonia, carbon dioxide, and water was undertaken. For this work the two gases, ammonia and carbon dioxide, were separately measured by means of calibrated orifice meters; the carbon dioxide was then passed through a saturator containing water at such a temperature that the desired quantity of water was carried along with the gas. The ammonia and humidified carbon dioxide were then led through a chamber and intimately mixed at such a temperature that no condensation occurred. From the mixing chamber the gases entered the condenser where the gas mixture came into contact with the cold condenser wall and deposited out in a layer that was continuously scraped off by a blade revolving at about 50 r. p. m. The condensate was allowed to fall into a hopper provided at the lower end of the tube.

A series of experiments were made with different rates of flow of gas into the condenser and different percentages of water in the gas. In each case the ratio of the volumes of ammonia to carbon dioxide was 2 : 1 as in ammonium carbamate. Results of these experiments are graphically shown in Fig. V. Examination of these curves reveals a characteristic relation between the rate of flow of the gases into the condenser and the efficiency of condensation. With a fixed percentage of water each curve shows a definite maximum efficiency which decreases when the rate of gas flow is raised or lowered. It is probable that this region of maximum efficiency is a function of the turbulence of the gases in the condenser and of the space velocity. It is also noteworthy that the efficiency is dependent on the water content up to a limiting value of about 1 per cent. The curves comprising Fig. VI show the effect of the rate of gas flow on the capacity, or hourly production, of the condenser. It is seen that with a fixed water percentage the capacity increases to a constant

value which represents the maximum output of ammonium carbamate with a specified water content regardless of the amount of gas sent into the condenser. Sufficient data have been collected from these experiments to afford a basis for an approximate calculation of the efficiency and capacity of larger condensers of the same general type.

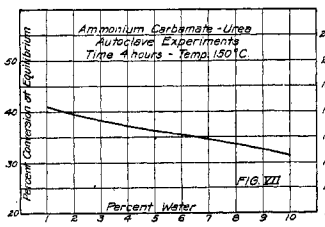


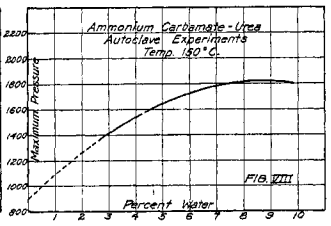


USE OF AMMONIUM CARBAMATE BRIQUETS—In all other processes of a similar nature, and in the several German patents on the process, it is apparently necessary to cool down the autoclave before each introduction of the charge. The volatility of ammonium carbamate and its high vapor pressure at elevated temperatures served to increase the difficulties. Finally, however, the idea of forming carbamate into a briquet of such a size as to enter the autoclave easily was adopted. Experiments on briquetting the charge showed that the material was well suited to the production of strong and easily handled briquets even when subjected to the small pressures available in the simple briquetting press that was assembled for these experiments. A test of loading the autoclave, previously heated to the working temperature, 150° C., with one of these briquets was then made. The entire practicability of this method of loading was demonstrated in an apparatus that was not entirely suitable for a fair test since the operation of closing the autoclave after the introduction of the charge was unnecessarily slow. With a properly designed rapid closing head, no difficulty should be experienced in introducing the charge without cooling the autoclave.

Experiments were then continued. The results of the glass tube experiments were substantiated, the yield of urea being consistently in the region of 40 per cent; that is, 40 per cent of the ammonia originally present in the charge of carbamate was converted to urea in the course of approximately 4 hrs. In one experiment a conversion of 41.1 per cent was obtained.

CONVERSION EXPERIMENTS—Examination of the vapor pressure curve in Fig. IV shows the high pressures that the autoclave in which the conversion reaction is carried out





must withstand. Consequently, the autoclave used in these experiments was tested to a pressure of 2500 lbs. per sq. in. previous to its use. The working pressure was calculated to be between 1200 and 1800 lbs. per sq. in. It was known that ammonium carbamate under the conditions of the conversion attacks steel. The parts coming into contact with the charge were therefore protected by a thick layer of tin.

The main body of the autoclave was a section of extra heavy steel pipe 18 in. long and 4.75 in. inside diameter. The pipe was threaded at both ends to receive flanges, to which in turn were bolted the top and bottom flanges that closed the openings at each end. A steam jacket around the pipe and suitable means for measuring the pressure and temperature of the charge were provided. The capacity of the finished autoclave was 0.174 cu. ft. or 4.93 liters, and it was capable of containing 12 lbs. or 5500 g. of ammonium carbamate.

EFFECT OF WATER ON THE CONVERSION

The effect of water on the conversion reaction was first studied, since it was necessary to know the limits within which good yields could be obtained. Autoclave charges were prepared containing percentages of water ranging from 1 to 10. These charges were carried through the conversion reaction, and the yield was noted in each case. The results are shown graphically in Fig. VII. As was expected, the addition of water to the system

$$(NH_3)_2CO_2 \rightleftharpoons CO(NH_2)_2 + H_2O$$

resulted in a partial reversal of the reaction and a consequent decrease in the percentage of ammonia converted to urea. The figure shows that each per cent of water added lowered the conversion approximately 1 per cent. There is, therefore, considerable latitude permissible in the operation of the condenser, since variations of several per cent in the water content of the ammonium carbamate cause only a small loss in the conversion.

EFFECT OF TEMPERATURE ON THE CONVERSION

The temperature at which the conversion reaction is carried out was shown by the preliminary experiments to have a marked influence on the equilibrium. A study of this factor was next made. Two charges, each containing 7.5 per cent of water, were autoclaved; one was heated at approximately 150° C. for 4 hrs., the other at approximately 140° C. for the same period. The yields were 34 and 19.75 per cent, respectively. These very significant results indicate that the reaction is endothermic and is probably accompanied by an appreciable heat change. It is, therefore, very desirable to maintain as high a temperature as possible during the course of the conversion. The limitation on the extent to which the temperature may be increased is evident from the vapor pressure curve already referred to (Fig. IV) and involves mechanical considerations regarding the strength of the autoclave.

EFFECT OF WATER ON THE EQUILIBRIUM PRESSURE

The experiments to determine the effect of water on the equilibrium showed that the maximum pressure of the system was dependent on the original water content of the charge. This relation is shown in Fig. VIII. Matignon and Frejacques[13] while working with dry carbamate obtained a pressure of 55.09 atmospheres (810 lbs. per sq. in.) at 150° C. This is close to the value, approximately 900 lbs. per sq. in., obtained by an extrapolation of the curve in Fig. VIII to 0 per cent water. It may be noted that an increase in the percentage of water is accompanied by an increase in the total pressure of the charge. A possible explanation of this surprising fact is that a change in the gaseous equilibrium results, due to a change in composition of the liquid phase. As the conversion proceeds, water is formed and, if we may make the somewhat doubtful assumption that increased percentages of ammonia are being removed from the gas phase because of its greater solubility in water, we must expect an increased total pressure as the equilibrium adjusts itself by an increased partial pressure of carbon dioxide.

It will be noted that the pressures obtained are of the same magnitude as those used in the Haber process for the synthe-

[13] *Compt. rend.*, **171** (1920), 1003.

sis of ammonia. The problem of designing apparatus to operate at these pressures is, however, much simpler since we are dealing with a much lower temperature and with heavier gases, and consequently the question of the porosity of metals to gases does not enter. Moreover, it is necessary to maintain this high pressure only in one stage of the process and not in pipe connections where ordinarily great difficulties arise. Furthermore, it is necessary to use autoclaves of small diameter in order to cause rapid transfer of heat through the charge, and therefore the difficulties of holding the pressure are much reduced. Only mechanical considerations limit the height of the autoclave.

Distillation of Autoclave Sludge

One step in the process still to be investigated was the distillation of the autoclave sludge, to separate the unconverted ammonium carbamate and condense it for further use in the process. For these experiments actual sludges, formed by the conversion of the carbamate charge, were discharged into the still.

The composition of the sludges was approximately the same for all distillation experiments; 40 per cent of the total ammonia was in the form of urea, and the remainder was combined with carbon dioxide in the proportion of two moles of ammonia to one of carbon dioxide. A quantity of water equivalent in moles to the quantity of urea was also present.

The sludge was released slowly from the autoclave into the still and cooled to about 57° to 59° C. In order to insure uniform composition in all parts of the sludge and to facilitate the escape of vapor, the still was equipped with a stirring device. Fig. IX shows the complete installation. The still was provided with a jacket and fitted up so that either cooling water or steam could be circulated.

The results of the conversion experiments indicated that about 40 per cent of the ammonia would be removed from each charge as urea. Assuming that the remaining 60 per cent could be recovered by distillation and condensation, it became necessary to make up this deficiency during the formation of the new autoclave charge. The most direct method was to introduce the "make-up" gases into the gas stream distilling from the sludge and thus utilize the same condenser for both purposes—recovery and "make-up" of the deficiency. This procedure was thoroughly tested.

DISTILLATION EXPERIMENTS—In the first experiments on the distillation of sludges the gases were allowed to pass over into the condenser as a result of their own vapor pressure. Additional or "make-up" ammonia and carbon dioxide were mixed with these vapors just before their entrance into the condenser. The course of the distillation could be followed from the results of analyses of the sludge residue taken from time to time during the distillation. The amount of "make-up" gas was determined by metering the ammonia and carbon dioxide. The general conclusion from these experiments is that the rate of distillation as governed by the vapor pressure of the solution is too slow to be practicable. It is not possible to heat the solution to a sufficiently high temperature to give a satisfactory current of vapor, since above 80° urea decomposes on continued heating in solution. It was very evident that some carrier for the gases must be provided to hasten the distillation at lower temperatures.

DISTILLATION WITH CARBON DIOXIDE—The selection of carbon dioxide as the carrier gas was largely due to its relative cost as compared with ammonia. Under the conditions of operation it seemed probable that a small fraction of the carrier gas would be lost, but the excess of carbon dioxide in the condenser would effect a higher percentage of ammonia utilization. Consequently, the use of carbon dioxide as a carrier gas is justified. In this connection it may be well to refer to the possibility of recirculating the gases coming out of the condenser instead of passing them into acid for the recovery of uncondensed ammonia. This recirculation would effect a saving of both carbon dioxide and ammonia, and deserves consideration. No attempt was made in this work to test out the practicability of recirculation.

In these distillation experiments, the apparatus was arranged so that carbon dioxide could be forced through the liquid sludge and then through the jacketed pipe leading to the condenser. A tube, connected to the vent in the hopper of the condenser and dipping into water, gave an indication of the volume of gas passing through the system without con-

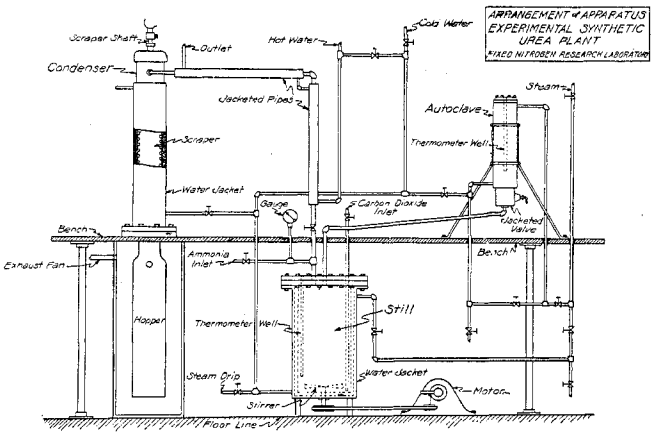


FIG. IX

densing. The flow of carbon dioxide was regulated so that this volume of escaping gas was very small. Several sludges were distilled in a stream of carbon dioxide and without adding any "make-up" ammonia in order to test the efficiency of the carrying agent. Results showed that all but a few per cent of the ammonia could be removed from the liquid sludge when carbon dioxide was used as a carrier and that complete condensation of the ammonia distilled off could be obtained under proper conditions. The rate of distillation and the smoothness of the heating curve of the sludge were found to be important factors bearing on the efficiency of condensation. The rate of distillation is of course governed by the capacity of the condenser. From Fig. VI we see that the maximum capacity at 100 per cent efficiency is about 700 g. per hr. The autoclave has a capacity of about 4500 g. in 4 hrs. or 1125 g. per hr.—very nearly twice the capacity of the condenser. It is to be expected that the preparation of an autoclave charge cannot therefore be efficiently carried out in 4 hrs. with the apparatus described. These experiments indicated that it was possible to condense completely the vapor distilling from a sludge.

The sludges have a boiling point, or region, where the distillation will proceed regularly and uniformly. If superheating is attempted it is to be expected that control of the flow of gas will be difficult. We have found that this boiling range is at about 57° to 59° C.; if this temperature is maintained throughout most of the distillation a steady stream of vapor can be passed into the condenser. When most of the gaseous constituents of the sludge have been distilled off it is necessary gradually to increase the temperature until about 80° C. is reached. With these results obtained, the final step of the investigation was to combine the use of the carrier and the addition of "make-up" ammonia.

It can be seen that continuous operation of this process is possible when the capacities of the autoclave and condenser are the same; that is, the condenser must produce during the period of conversion just as much ammonium carbamate as the autoclave requires for one charge. Since continuous